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(54) Abstract Title
Polymerisable composition comprising epoxy compounds

(57) The invention relates to a polymerizable composition comprising epoxy compounds, characterized in that said composition comprises the following components:

a) component A comprising at least one chiral polymerizable mesogenic compound having one terminal polymerizable epoxy group,
b) component B comprising at least one achiral polymerizable mesogenic compound having one terminal polymerizable epoxy group,
c) optionally component C comprising at least one polymerizable mesogenic compound having two or more terminal polymerizable epoxy groups,
d) optionally component D comprising one or more polymerizable non-mesogenic compounds having two or more terminal polymerizable epoxy groups,
e) optionally component E comprising one or more chiral dopants, and
f) an initiator component F comprising at least one polymerization initiator.

to linear and crosslinked polymers obtainable by in-situ polymerisation of said composition, and to the use of said composition for the preparation of anisotropic polymers or polymer films for decorative pigments, security applications, electrooptical devices, colour filters and adhesives.

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Polymerizable Composition Comprising Epoxy Compounds

The invention relates to a polymerizable composition comprising epoxy compounds, characterized in that said composition comprises the following components:

a) component A comprising at least one chiral polymerizable mesogenic compound having one terminal polymerizable epoxy group,

b) component B comprising at least one achiral polymerizable mesogenic compound having one terminal polymerizable epoxy group,

c) optionally component C comprising at least one polymerizable mesogenic compound having two or more terminal polymerizable epoxy groups,

d) optionally component D comprising one or more polymerizable non-mesogenic compounds having two or more terminal polymerizable epoxy groups,

e) optionally component E comprising one or more chiral dopants, and

f) an initiator component F comprising at least one polymerization initiator.

The invention further relates to linear and crosslinked polymers obtainable by in-situ polymerisation of said composition and to the use of said composition for the preparation of anisotropic polymers or polymer films for decorative pigments, security applications, electrooptical devices, colour filters and adhesives.

Polymerizable mesogenic compounds can be polymerized in situ when being macroscopically oriented in their liquid crystalline state to give anisotropic linear or crosslinked polymers or polymer films with a uniform orientation of high quality. Such films can be used for example as optical elements like dichroic polarizers, which are described e.g. in EP 0 397 263, orientation layers (EP 0 467 456) or optical waveguides (EP 0 331 233).

Anisotropic polymer films with a chiral liquid crystalline phase can be obtained from polymerizable chiral mesogenic compounds. They are useful in particular as optical retardation films or reflective polarizers, like for example described in EP 0 606 940.

The polymerizable mesogenic compounds that are most commonly used in prior art for the above applications are mesogenic acrylates. However, anisotropic polymer films prepared by polymerization of mesogenic acrylates or mixtures thereof, in particular of mixtures comprising mesogenic diacrylates, often exhibit a high brittleness. Further to that, polymer films obtained from mesogenic acrylates often show poor adhesion to other films or to substrates.

This is a disadvantage for several applications, in particular for optical uses, wherein thin films with high flexibility are needed for the assembly of optical devices such as e.g. flat panel displays.

Furthermore, in the above mentioned applications the anisotropic polymer films are often laminated to other optical elements, or a number of single anisotropic polymer films are laminated together to form a multilayer. For this purpose, usually adhesive layers, such as layers of PSA (pressure sensitive adhesive) are applied on top of the anisotropic polymer films and optical elements in order to glue them together, which often negatively affects the optical properties of the final product.

Thus, there is a considerable demand for polymers and polymerizable compositions that are suitable for the preparation of

anisotropic polymer films which exhibit a high flexibility, show strong adhesion to other films and substrates and, in the ideal case, can act as their own adhesive.

Furthermore, regarding the broad range of applications for polymerizable mesogenic compounds and compositions it is desirable for the expert to have available further materials of this type which are easy to synthesize and fulfill the various requirements as described above.

One of the aims of the present invention is to provide a polymerizable composition for the preparation of anisotropic polymers and anisotropic polymer films which do not have the disadvantages of the polymers of prior art discussed above.

Another aim of the present invention is to extend the pool of polymerizable mesogenic compounds and mixtures available to the expert. Other aims of the present invention are immediately evident to the person skilled in the art from the following detailed description.

It has been found that this aim can be achieved by providing a polymerizable composition comprising polymerizable mesogenic epoxy compounds according to the present invention. In particular, it has been found that it is possible to prepare anisotropic polymer films exhibiting strong bonding forces, which can even glue substrates together, from a mixture comprising the components A) to F) according to the present invention.

The German Application DE 195 04 224 discloses a polymer gel comprising a low molar mass liquid crystalline material and a polymer network, wherein the network is obtainable from a precursor material comprising a chiral monofunctional and an achiral difunctional polymerizable epoxy compound. However, the DE 195 04 224 gives no hint to strong bonding polymers that can glue substrates together and are obtainable from mixtures like those of the present invention.

The terms polymerizable mesogenic compound or polymerizable liquid crystalline compound as used in the foregoing and the following comprise compounds with a rod-shaped, board-shaped or disk-shaped mesogenic group, i.e. a group with the ability to induce mesophase or liquid crystalline phase behaviour in a compound comprising said group. Such compounds do not necessarily have to exhibit a liquid crystalline phase themselves. It is also possible that these compounds show mesophase behaviour only in mixtures with other compounds or when the polymerizable mesogenic compounds or mixtures thereof are polymerized.

Preferably the polymerizable mesogenic compounds show liquid crystalline phase behaviour themselves.

One of the objects of the present invention is a composition comprising epoxy compounds, characterized in that said composition comprises the following components:

a) component A comprising at least one chiral polymerizable mesogenic compound having one terminal polymerizable epoxy group,

b) component B comprising at least one achiral polymerizable mesogenic compound having one terminal polymerizable epoxy group,

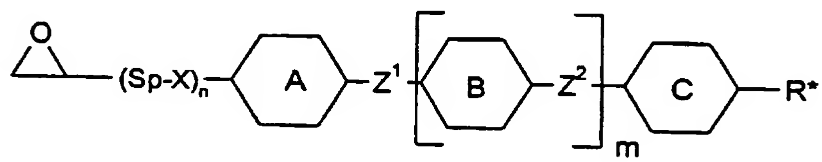
c) optionally component C comprising at least one polymerizable mesogenic compound having two or more terminal polymerizable epoxy groups,

d) optionally component D comprising one or more polymerizable non-mesogenic compounds having two or more terminal polymerizable epoxy groups,

e) optionally component E comprising one or more chiral dopants, and

f) an initiator component F comprising at least one polymerization initiator.

In a preferred embodiment of the present invention component A comprises at least one compound of formula I:



I

wherein

the rings A, B and C denote each independently 1,4-cyclohexylene, 1,4-cyclohexenylene, or 1,4-phenylene that is optionally substituted by one or two halogen atoms, cyano groups, or alkyl, alkoxy or alkanoyl groups with 1 to 4 C-atoms that may be unsubstituted, mono- or polysubstituted by F or Cl,

Z^1 and Z^2 are each independently $-CH_2CH_2-$, -COO-, -OCO-, $-OCH_2-$, $-CH_2O-$, -CH=CH-COO-, -OCO-CH=CH-, -CH=CH-, -C≡C- or a single bond,

L^1 and L^2 are each independently H or F,

m is 0, 1 or 2,

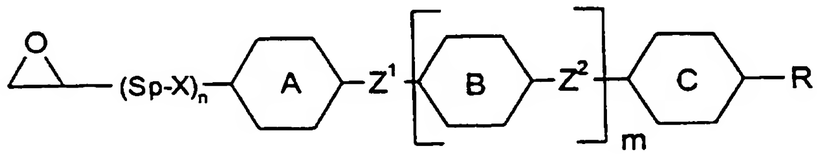
n is 0 or 1,

Sp is a spacer group having 1 to 18 C atoms,

X is -O-, -S-, -CO-, -COO-, -OCO-, -O-COO-, -CO-S-, -S-CO- or a single bond, and

R* is a chiral radical having at least one chiral C atom.

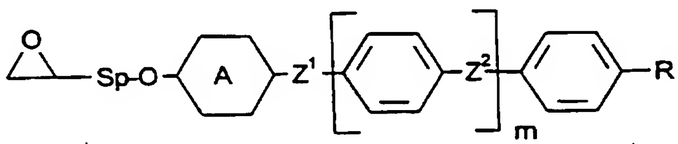
In another preferred embodiment of the present invention the component B comprises at least one compound of formula II:



II

wherein A, B, C, Sp, X, Y, Z^1, Z^2, m and n have the meaning given for formula I, and R is an achiral radical having up to 16 C atoms.

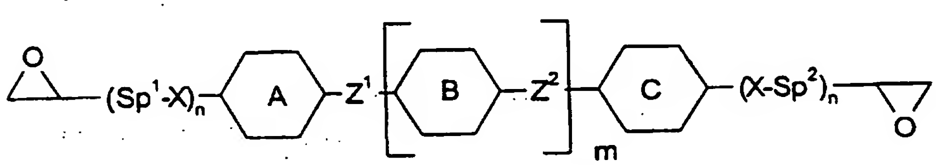
Particularly preferred compounds of formula II are those of formula IIa



IIa

wherein A, Z^1, R, n, m and Sp have the meaning given in formula II and Z^2 is -COO- or a single bond.

In another preferred embodiment of the present invention component C comprises at least one compound of formula III:

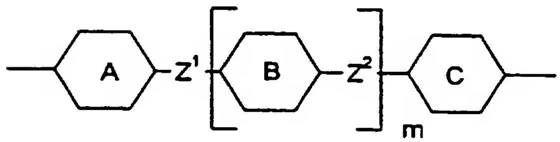


III

wherein A, B and C, X, Y, Z^1, Z^2, m and n have the meanings given for formula I as described above and Sp^1 and Sp^2 each independently have the meaning given for Sp in formula I. Especially preferred are compounds of formula III wherein Sp^1 is different from Sp^2.

The novel compounds of formula I, II and III and their preferred subformulae, in particular the novel compounds of formula IIa, are another object of the present invention.

Particularly preferred mesogenic compounds of the formula I, II and III are those wherein the mesogenic group



is in each case independently a two-ring, three-ring or four-ring group.

Compounds of formula I, II and III with mesogenic groups comprising two rings or three rings are particularly preferred.

Halogen is preferably F, Cl or Br, especially preferably F.

Of the preferred compounds containing a substituted 1,4-phenylene group very particularly preferred are those substituted by F, Cl or an optionally fluorinated alkyl, alkoxy or alkanoyl group with 1 to 4 C atoms.

A smaller group of particularly preferred mesogenic groups of the formulae I, II and III is listed below. For reasons of simplicity, PheL is 1,4-phenylene, which is substituted in 2- and/or 3-position with L, wherein L denotes halogen, a cyano or nitro group or an alkyl, alkyloxy or alkanoyl group having 1 to 7 C atoms wherein one or more H atoms may be substituted by F or Cl, and Cyc is 1,4-cyclohexylene.

Z^1 and Z^2 in these groups have the meaning given in formula I as described above and below.

Preferred two-ring mesogenic groups are those of the following formulae:

-Phe-Z^1-Phe- 1-1
-Phe-Z^1-PheL- 1-2
-PheL-Z^1-PheL- 1-3

-Phe-Z^1-Cyc-	1-4
-Cyc-Z^1-Phe-	1-5
-Cyc-Z^1-PheL-	1-6
-Cyc-Z^1-Cyc-	1-7

In the formulae 1-1 to 1-7, Z^1 is preferably -COO-, -O-CO-, -CH_2CH_2- or a single bond.

Of the preferred mesogenic groups of formula 1-1 to 1-7, those of formula 1-1 to 1-4 are particularly preferred.

Preferred three-ring mesogenic groups are those of the following formulae:

-Phe-Z^1-Phe-Z^2-Phe-	2-1
-PheL-Z^1-Phe-Z^2-Phe-	2-2
-Phe-Z^1-Phe-Z^2-PheL-	2-3
-Phe-Z^1-PheL-Z^2-Phe-	2-4
-PheL-Z^1-Phe-Z^2-PheL-	2-5
-PheL-Z^1-PheL-Z^2-PheL-	2-6
-Phe-Z^1-PheL-Z^2-PheL-	2-7
-PheL-Z^1-PheL-Z^2-Phe-	2-8
-Phe-Z^1-Phe-Z^2-Cyc-	2-9
-PheL-Z^1-Phe-Z^2-Cyc-	2-10
-Phe-Z^1-Cyc-Z^2-Phe-	2-11
-PheL-Z^1-Cyc-Z^2-Phe-	2-12
-Cyc-Z^1-Cyc-Z^2-Phe-	2-13
-Cyc-Z^1-Phe-Z^2-Phe-	2-14

Of the preferred mesogenic groups of formula 2-1 to 2-14, those of formula 2-1 to 2-4, 2-9 and 2-10 are particularly preferred.

In particular preferred are the compounds of formulae 2-1 to 2-14 in which Z^1 is -COO- and Z^2 is -OCO- or both Z^1 and Z^2 are a single bond.

Of these preferred compounds very particularly preferred are those of formula 2-4, wherein PheL is especially preferably a 1,4-phenylene group substituted by an optionally fluorinated alkyl, alkoxy or alkanoyl group with 1 to 4 C atoms.

Preferred four-ring mesogenic groups are those of the following formulae:

-Phe-Z^1-Phe-Z^2-Phe-Z^2-Phe-	3-1
-Phe-Z^1-Phe-Z^2-Phe-Z^2-PheL-	3-2
-Phe-Z^1-Phe-Z^2-PheL-Z^2-Phe-	3-3
-Phe-Z^1-PheL-Z^2-Phe-Z^2-Phe-	3-4
-PheL-Z^1-Phe-Z^2-Phe-Z^2-Phe-	3-5
-Phe-Z^1-PheL-Z^2-PheL-Z^2-Phe-	3-6
-Phe-Z^1-Phe-Z^2-Phe-Z^2-Cyc-	3-7
-Phe-Z^1-Cyc-Z^2-Phe-Z^2-Phe-	3-8
-Phe-Z^1-Cyc-Z^2-Phe-Z^2-Cyc-	3-9
-Cyc-Z^1-Phe-Z^2-Phe-Z^2-Cyc-	3-10
-Phe-Z^1-PheL-Z^2-Phe-Z^2-Cyc-	3-11
-PheL-Z^1-PheL-Z^2-Phe-Z^2-Cyc-	3-12

Of the mesogenic groups of formula 3-1 to 3-12, those of formula 3-1 to 3-4, 3-7 and 3-10 are preferred. Especially preferred are the mesogenic groups of formula 3-1 to 3-4.

In the mesogenic groups of the formulae 3-1 to 3-12, at least one of the groups Z^1 or Z^2 is very particularly preferably a single bond.

In the formulae 1-1 to 1-7, 2-1 to 2-14 and 3-1 to 3-12, L is preferably F, Cl, CN, NO_2, CH_3, C_2H_5, OCH_3, OC_2H_5, $COCH_3$, COC_2H_5, CF_3, OCF_3, $OCHF_2$, OC_2F_5, in particular F, Cl, CN, CH_3, C_2H_5, OCH_3, $COCH_3$ and OCF_3 , most preferably F, CH_3, OCH_3 and $COCH_3$.

In the compounds of formula I, R* is preferably selected according to the following formula IV:

$$X^1\text{-}Q^1\text{-}\overset{*}{C}H\text{-}Q^2 \qquad \text{IV}$$
$$\qquad\quad |$$
$$\qquad\quad Q^3$$

wherein

X^1 has the meaning given for X,

Q^1 is an alkylene or alkylene-oxy group with 1 to 10 C atoms or a single bond,

Q^2 is an alkyl or alkoxy group with 1 to 10 C atoms which may be unsubstituted, mono- or polysubstituted by halogen or CN, it being also possible for one or more non-adjacent CH_2 groups to be replaced, in each case independently from one another, by -C≡C-, -O-, -S-, -NH-, -N(CH_3)-, -CO-, -COO-, -OCO-, -OCO-O-, -S-CO- or -CO-S- in such a manner that oxygen atoms are not linked directly to one another, or alternatively has the meaning given for P-Sp-,

Q^3 is halogen, a cyano group or an alkyl or alkoxy group with 1 to 4 C atoms different from Q^2.

Preferred chiral groups are 2-butyl (=1-methylpropyl), 2-methylbutyl, 2-methylpentyl, 3-methylpentyl, 2-ethylhexyl, 2-propylpentyl, 2-octyl, in particular 2-methylbutyl, 2-methylbutoxy, 2-methylpentoxy, 3-methylpentoxy, 2-ethylhexoxy, 1-methylhexoxy, 2-octyloxy, 2-oxa-3-methylbutyl, 3-oxa-4-methylpentyl, 4-methylhexyl, 2-nonyl, 2-decyl, 2-dodecyl, 6-methoxyoctoxy, 6-methyloctoxy, 6-methyloctanoyloxy, 5-methylheptyloxycarbonyl, 2-methylbutyryloxy, 3-methylvaleroyloxy, 4-methylhexanoyloxy, 2-chlorpropionyloxy, 2-chloro-3-methylbutyryloxy, 2-chloro-4-methylvaleryloxy, 2-chloro-3-methylvaleryloxy, 2-methyl-3-oxapentyl, 2-methyl-3-oxahexyl, 1-methoxypropyl-2-oxy, 1-ethoxypropyl-2-oxy, 1-propoxypropyl-2-oxy, 1-butoxypropyl-2-oxy, 2-fluorooctyloxy, 2-fluorodecyloxy, for example.

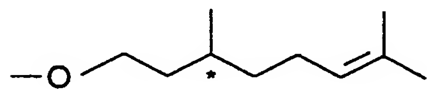
In another preferred embodiment of the present invention the chiral group R* is selected from the following groups:

an ethylenglycol derivative

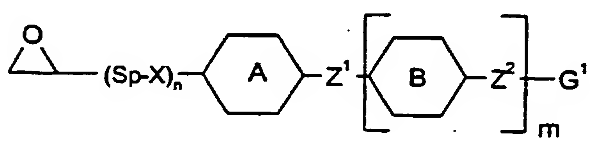
$$-O-\underset{*}{\overset{\overset{\displaystyle CH_3}{|}}{C}}HCH_2OR^1$$

wherein R^1 is an alkyl radical with 1 to 12 C atoms,

or a group based on citronellol.

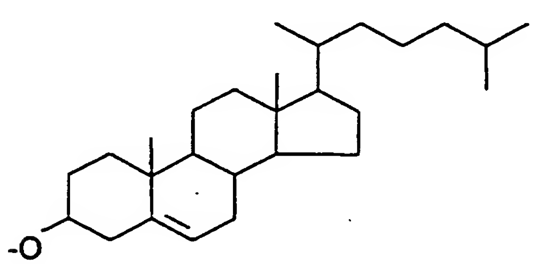


In another preferred embodiment of the present invention the compounds of formula I comprises a mesogenic or mesogenity supporting group having at least one center of chirality. These compounds are preferably selected according to formula Ia:

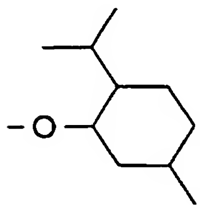


Ia

wherein Sp, X, m, n, A, B, Z^1 and Z^2 have the meaning given for formula I and G^1 is a terminal chiral group, such as for example a cholesteryl group,



a terpenoid radical, like e.g. disclosed in the WO 96/17901, particularly preferably a menthyl group, particularly preferably a menthyl group,



or a terminal chiral sugar derivative comprising a mono- or dicyclic radical with pyranose or furanose rings like, for example, a terminal group derived from the chiral sugars or sugar derivatives as disclosed e.g. in the international application WO 95/16007.

In the mesogenic compounds of the formula II, R is preferably an achiral alkyl radical which is unsubstituted or substituted by at least one halogen atom, it being possible for one or two non-adjacent CH_2 groups of these radicals to be replaced by -O-, -S-, O-CO-, -CO-O- or -O-CO-O- groups.

If R is an alkyl or alkoxy radical, i.e. where the terminal CH_2 group is replaced by -O-, this may be straight-chain or branched. It is preferably straight-chain, has 2, 3, 4, 5, 6, 7 or 8 carbon atoms and accordingly is preferably ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, ethoxy, propoxy, butoxy, pentoxy, hexoxy, heptoxy, or octoxy, furthermore methyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, methoxy, nonoxy, decoxy, undecoxy, dodecoxy, tridecoxy or tetradecoxy, for example.

Oxaalkyl, i.e. where one CH_2 group is replaced by -O-, is preferably straight-chain 2-oxapropyl (=methoxymethyl), 2- (=ethoxymethyl) or 3-oxabutyl (=2-methoxyethyl), 2-, 3-, or 4-oxapentyl, 2-, 3-, 4-, or 5-oxahexyl, 2-, 3-, 4-, 5-, or 6-oxaheptyl, 2-, 3-, 4-, 5-, 6- or 7-oxaoctyl, 2-, 3-, 4-, 5-, 6-, 7- or 8-oxanonyl or 2-, 3-, 4-, 5-, 6-,7-, 8- or 9-oxadecyl, for example.

In addition, mesogenic compounds of the formula II containing an achiral branched group R may occasionally be of importance as comonomers, for example, due to a reduction in the tendency towards crystallization. Branched groups of this type generally do not contain more than one chain branch. Preferred achiral branched groups are isopropyl, isobutyl (=methylpropyl), isopentyl (=3-methylbutyl), isopropoxy, 2-methylpropoxy and 3-methylbutoxy.

As for the spacer group Sp, Sp^1 and Sp^2 in formulae I, II and III, all groups can be used that are known for this purpose to the skilled in the art. The spacer groups Sp, Sp^1 and/or Sp^2 are preferably linked to the polymerizable epoxy group by an ester or ether group or a single bond. The spacer groups Sp, Sp^1 and/or Sp^2 are preferably a linear or branched alkylene group having 1 to 20 C atoms, in particular 1 to 12 C atoms, in which, in addition, one or more non-adjacent CH_2 groups may be replaced by -O-, -S-, -NH-, -N(CH_3)-, -CO-, -O-CO-, -S-CO-, -O-COO-, -CO-S-, -CO-O-, -CH(halogen)-, -CH(CN)-, -CH=CH- or -C≡C-.

Typical spacer groups are for example -$(CH_2)_o$-, -$(CH_2CH_2O)_r$-CH_2CH_2-, -CH_2CH_2-S-CH_2CH_2- or -CH_2CH_2-NH-CH_2CH_2-,with o being an integer from 2 to 12 and r being an integer from 1 to 3.

Preferred spacer groups are ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, nonylene, decylene, undecylene, dodecylene, octadecylene, ethyleneoxyethylene, methyleneoxy-butylene, ethylene-thioethylene, ethylene-N-methyl-iminoethylene and 1-methylalkylene, for example.

In a preferred embodiment of the invention the spacer group Sp in the compounds of formula I and/or III is a chiral group of the formula V:

$$\begin{array}{c} Q^1\text{-}\overset{*}{C}H\text{-}Q^4\text{-} \\ | \\ Q^3 \end{array} \qquad \text{V}$$

wherein

Q^1 and Q^3 have the meanings given in formula IV and

Q^4 is an alkylene or alkylene-oxy group with 1 to 10 C atoms or a single bond, being different from Q^1.

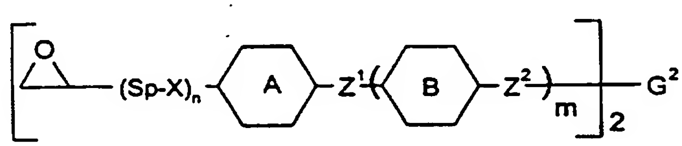
In particular preferred are compounds of formula I, II and/or III wherein n is 1.

In a preferred embodiment of the invention, the anisotropic polymers are copolymers obtained by copolymerizing mixtures comprising compounds of formula I, II and/or III wherein n is 0 and compounds of formula I wherein n is 1.

In a preferred embodiment of the present invention the component C comprises at least one chiral mesogenic compound having two or more terminal epoxy groups as polymerizable groups.

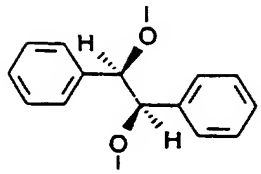
Preferred compounds of component C according to this preferred embodiment are compounds of formula III wherein at least one of the spacer groups Sp^1 and Sp^2 is a chiral group according to formula V as described above.

Further preferred are compounds of component C according to this preferred embodiment that are selected of formula IIIa

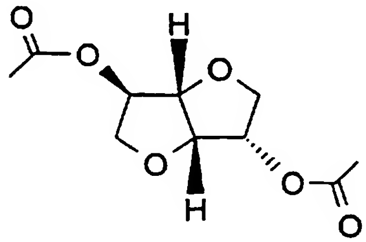


IIIa

wherein X, m, n, A, B, Z^1 and Z^2 have each independently the meaning given for formula I, and G^2 is a bivalent chiral group, like for example a (S,S)- or (R,R)-hydrobenzoin group



or a bivalent chiral sugar, sugar derivative or another bivalent chiral radical, as disclosed e.g. in the international application WO 95/16007, especially preferably a group based on 1,4:3,6-Dianhydro-D-sorbitol:



In case G^2 is a group based on 1,4:3,6-Dianhydro-D-sorbitol as diclosed above, in case of m = 1 Z^2 and/or in case of m = 0 Z^1 is preferably denoting -CH=CH- .

The polymerizable mesogenic and non-mesogenic epoxy compounds according to the present invention can be prepared by methods which are known per se and which are described, for example, in standard works of organic chemistry such as, for example, Houben-Weyl, Methoden der organischen Chemie, Thieme-Verlag, Stuttgart. Furthermore the inventive compounds according to formula I, II and III can be prepared according to or in analogy to methods described in DE 195 04 224.

In a preferred embodiment of the present invention the polymerizable composition comprises

a) 2 to 75 % , preferably 5 to 70 %, in particular 7 to 65 % by weight of the chiral component A ,

b) 10 to 90 % , preferably 12 to 80 %, in particular 15 to 70 % by weight of the achiral component B,

c) 0 to 60 %, preferably 5 to 55 %, in particular 10 to 45 % by weight of the component C,

d) 0 to 20 %, preferably 2 to 15 %, in particular 3 to 10 % by weight of the component D,

e) 0 to 15 %, preferably 1 to 10 % by weight of the chiral dopant component E, and

f) 0.01 to 10 % , preferably 0.1 to 5 % by weight of the initiator component F.

In a particularly preferred embodiment of the invention the component B of the polymerizable mixture comprises at least two different achiral polymerizable epoxy compounds, preferably selected of formula II .

In another preferred embodiment the polymerizable composition comprises two to eight, in particular three to six different achiral polymerizable epoxy compounds.

The amount of each of the achiral polymerizable epoxy compounds is preferably 5 to 80, in particular 10 to 70, very preferably 15 to 65 % by weight of the total mixture.

In another preferred embodiment of the present invention the polymerizable composition contains less than 10 % by weight, very preferably no compounds of component C.

The chiral polymerizable epoxy compounds of component A are inducing chiral mesophase behaviour, like e.g. a chiral smectic or a chiral nematic (cholesteric) phase, in the inventive polymerizable compositions, and in the anisotropic polymers or polymer films obtainable from these compositions.

Especially preferred are inventive polymerizable compositions and inventive anisotropic polymers or polymer films that exhibit a cholesteric phase.

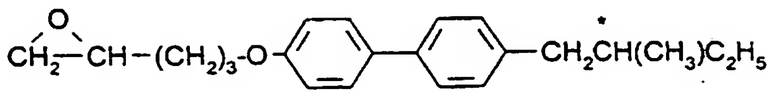
In a preferred embodiment of the present invention the chiral polymerizable epoxy compounds of component A are selected of formula I.

In a preferred embodiment of the present invention component A, C and/or E comprise at least one chiral compound with a high helical twisting power. The helical twisting power **HTP** is the ability of a chiral compound to induce or enhance a helically twisted molecular structure in a liquid crystalline medium. It is related to the concentration **c** of the chiral compound in the liquid crystalline medium and to the pitch **p** of the molecular helix in the first approximation, which is sufficient for most practical applications, according to the following equation:

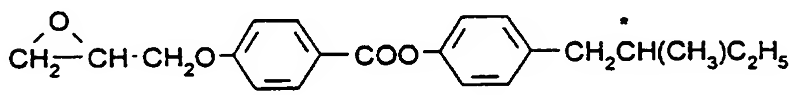
$$p = \frac{1}{HTP} \cdot \frac{1}{c} \qquad (1)$$

Thus, in case of chiral compounds with a high value of the HTP low amounts of these compounds are sufficient to obtain a short cholesteric pitch. Therefore, if component A, C or E comprise chiral compounds with a high HTP, these compounds do not necessarily have to be liquid crystalline. It is also possible to use compounds that are mesogenic - in line with the definition given above in the introduction - but do not exhibit a liquid crystalline phase per se, without significantly altering the mesogenic phase behaviour of the composition and/or the resulting anisotropic polymer film.

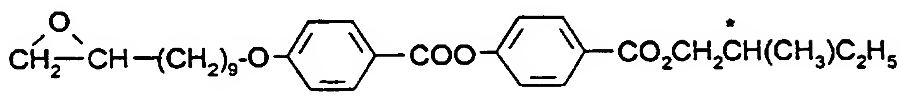
Thus, in another preferred embodiment according to the present invention the chiral polymerizable epoxy compounds of component A are non-liquid crystalline compounds. Examples for chiral polymerizable compounds that are mesogenic but non-liquid crystalline are the following compounds.



phase behaviour: K 48 I



phase behaviour: K 38 I



phase behaviour: K 44 I

It is also possible to add one or more chiral dopants of component E with a high HTP to the inventive polymerizable composition. alternatively or in addition to chiral polymerizable compounds of component A and C.

The chiral dopants of component E with a high HTP are preferably selected of chiral compounds with a HTP of > 15, in particular > 20, very preferably > 30 μm^{-1}.

Examples for high HTP dopants that are preferably used for component E are chiral non-polymerizable mesogenic or non-mesogenic compounds comprising one or more radicals selected of the following groups

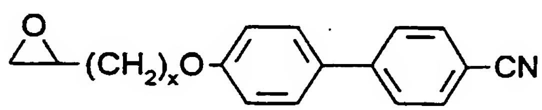
- terminal groups R* of formula IV,
- terminal groups G^1 as defined above,
- bivalent spacer groups or formula V, and
- bivalent groups G^2 as defined above.

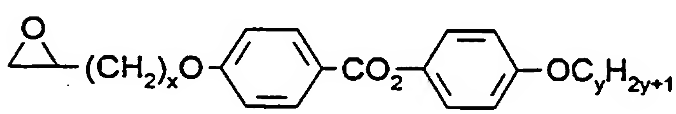
Suitable high HTP dopants and their synthesis are disclosed e.g in the WO 98/00428 or GB 2,279,659.

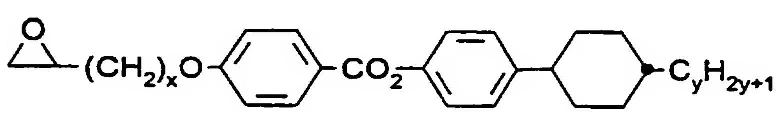
Furthermore, it is possible to use for component C chiral polymerizable mesogenic diepoxides that comprise one or more of the above mentioned chiral groups R*, Sp, G^1 and G^2 and may be liquid crystalline or not. These compounds are preferably selected of formula IIIa.

The helical pitch which is imported by the mesogenic or non-mesogenic chiral compounds into the polymerizable composition and/or the anisotropic polymers or polymer films according to the present invention is preferably from 0.1 to 2.5 μm, especially preferably 0.2 to 2 μm, in particular 0.25 to 1.8 μm. Particularly preferred are compositions exhibiting a helical pitch such that they reflect light in the visible and/or UV and/or IR wavelength range.

Typical examples of suitable compounds of component B are the following compounds:







wherein x and y are each independently integers from 1 to 12.

Another object of the present invention are linear and/or crosslinked anisotropic copolymers obtainable by in-situ (co)polymerisation of the compositions comprising components A, B, F and optionally C, D and E as described above and below.

Yet another object of the present invention is use of the compositions comprising components A, B, F and optionally C, D and E as described above and below for the preparation of anisotropic polymers or polymer films for decorative pigments, security applications, electrooptical devices, colour filters and adhesives.

Polymers or copolymers can be prepared from the inventive polymerizable mesogenic compounds for example by solution polymerization. Solution polymerization can be carried out e.g. by dissolving the polmyerizable material in a solvent like dichloromethane, THF or toluene together with AIBN (azobisisobutyronitrile) as polymerization initiator and heating for 24 hours at 30 to 60 °C.

In order to obtain polymer films with macroscopic uniform orientation, which is desired for most applications, polymers obtained e.g. by solution polymerization have to be aligned afterwards, for example by application of mechanical shear forces, electric or magnetic fields and/or high temperatures.

However, polymers can only be well aligned if they are not or only slightly crosslinked. On the other hand, highly crosslinked polymers, although difficult to align, are preferred in particular for optical applications, as they show higher thermal and mechanical stability and exhibit lower temperature dependence of their optical properties compared to slightly crosslinked or linear polymers.

Alternatively, polymer films with with macroscopic uniform orientation can be prepared from the inventive polymerizable epoxy compounds and compositions by coating the polymer precursor material onto a substrate, aligning it e.g. by conventional techniques, which can be easier achieved than for polymers, and freezing in the alignment by in-situ polymerization. This method yields particularly well aligned anisotropic polymer films. A detailed description of this method can be found in D.J.Broer et al., Makromol.Chem. **190**, 2255 ff. (1989).

The polymerizable liquid crystal compounds and compositions according to this invention are preferably prepared by in-situ polymerization as described in the foregoing and the following.

Polymerization of polymerizable mesogenic compounds or compositions comprising compounds with only one polymerizable functional group leads to linear polymers or copolymers, whereas in the presence of compounds with more than one polymerizable functional group crosslinked polymers are obtained.

In particular highly crosslinked polymers show very high thermal stability of the optical and mechanical properties, depending on the degree of crosslinking, when compared to linear polymers, which is preferred for several applications.

Linear or slightly crosslinked polymer films on the other hand show a higher flexibility and are therefore preferred for some applications.

Linear or crosslinked polymers or copolymers can be obtained for example by exposure of the inventive polymerizable compounds or compositions comprising a polymerization initiator component F to actinic radiation, wherein the initiator is absorbing at the wavelength of said radiation.

For example, one can use UV light and as initiator component F a photoinitiator that decomposes under UV irradiation to produce free radicals that start the polymerization reaction. In another preferred embodiment component F comprises at least one cationic photoinitiator that photocures with cations instead of free radicals. The polymerization may also be started by an initiator that decomposes when heated above a certain temperature.

Preferably a cationic photoinitiator is used for component F.

As a cationic photoinitiator for example the commercially available Cyracure UVI 6974 (from Union Carbide) can be used.

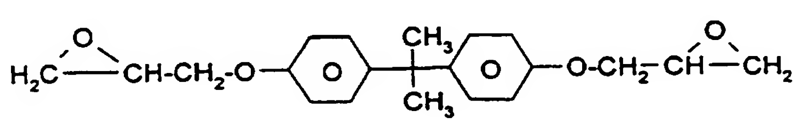
In addition to light- or temperature-sensitive initiators the compositions according to the present invention may also comprise one or more other suitable components such as, for example, catalysts, stabilizers, co-eacting monomers or surface-active compounds.

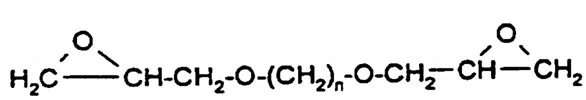
Further to the chiral dopant component E, it is possible to add a quantity of up to 10% by weight of a non-polymerizable liquid-crystalline material to adapt the optical properties of the polymer.

It is also further possible to add altematively or additionally up to 20% of a component D comprising one or more non mesogenic epoxy compounds with two or more polymerizable functional groups to increase crosslinking of the polymers.

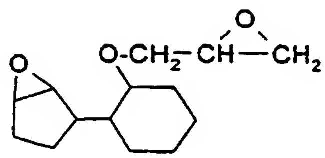
Typical examples for difunctional non mesogenic monomers are alkyldiepoxides with alkyl groups of 1 to 20 C atoms. Typical examples for non mesogenic monomers with more than two polymerizable groups are are trimethylpropanetriepoxide or pentaerythritoltetraepoxide.

Further examples of non-mesogenic epoxides can be taken from the "Handbook of Epoxy Resins" by H. Lee and K. Neville, McGraw-Hill, New York, 1967. Typical compounds of this type that are suitable for the inventive compositions are for example represented by the following formulae





n = 1-12



To prepare anisotropic polymer films with uniform orientation the inventive reactive mesogenic compounds or compositions, for example, are coated onto a substrate, aligned and cured by irradiation as described above. Alignment and curing are carried out in the mesophase of the reactive mesogenic compounds.

As a substrate for example a glass plate or a plastic film can be used. Preferably the substrate is a flexible plastic substrate, such as for example a polypropylene film, polyethyleneterephthalate (PET) film, polyvinylalcohol (PVA) film, polycarbonate (PC) film or triacetylcellulose (TAC) film. PET films are commercially available for example from ICI Corp. under the trade name Melinex. Isotropic or birefringent substrates can be used. In case the substrate is not removed from the coated film, preferably isotropic substrates are used. As a birefringent substrate for example an uniaxially stretched plastic film can be used.

To achieve uniform alignment, the film can be sheared for example by means of a doctor blade. In another preferred embodiment, a second substrate is put on top of the coated material. In this case, the shearing caused by putting together the two substrates is sufficient to give good alignment.

In some cases it is of advantage, and thus preferred, to apply a second substrate to exclude oxygen that may inhibit the polymerization. Alternatively the curing can be carried out under an atmosphere of inert gas, for example under a nitrogen atmosphere. In this case shearing of the mesogenic material prior to polymerization is necessary to cause sufficient alignment of the mesophase. When using a cationic photoinitiator oxygen exclusion is not needed, but water should preferably be excluded.

The compounds of the present invention are preferably used in mixtures with other reactive mesogenic compounds to give mixtures with low melting points. This is of importance especially when anisotropic polymer films are prepared. To obtain highly oriented films the polymerization is preferably carried out in the liquid crystal phase of the reactive liquid crystal mixture. Thus, by using mixtures of the compounds of this invention the polymerization temperature is lowered significantly and the polymerization process is made easier.

In another preferred embodiment, the polymerizable mixture, after having been coated on the substrate and optionally having been sheared, is annealed in its liquid crystal phase for a given period of time before being polymerized, in order to improve alignment.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to ist fullest extent. The following examples are, therefore, to be construed as merely illustrative and not limitative of the remainder of the disclosure in any way whatsoever.

In the foregoing and in the following examples, unless otherwise indicated, all temperatures are set forth uncorrected in degrees Celsius and all parts and percentages are by weight. The following abbreviations are used to illustrate the liquid crystalline phase behaviour of the compounds: K = crystalline; N = nematic; S = smectic; Ch = cholesteric; I = isotropic. The numbers between these symbols indicate the phase transition temperatures in degree Celsius.

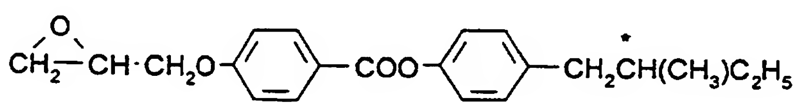
Unless explicitly stated otherwise, in the foregoing and the following the values of the helical twisting power HTP of a chiral compound refer

to a solution of the compound in a liquid crystalline host according to the equation HTP = $(p \cdot c)^{-1}$ in μm^{-1}, wherein p is the pitch of the molecular helix in μm and c is the concentration by weight of the chiral compound in the host in relative values (thus, e.g. a concentration of 1 % by weight is corresponding to a value of c = 0.01).

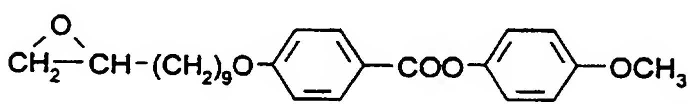
Example 1

The following mixture was formulated:

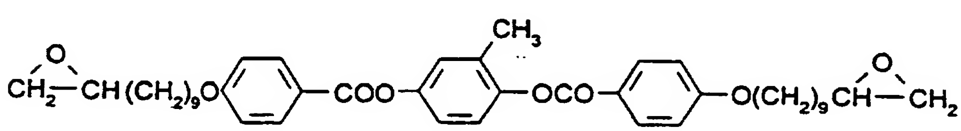
compound (1)	49.8 %
compound (2)	20.1 %
compound (3)	28.1 %
UVI 6974	2.0 %



(1)



(2)



(3)

The compounds (1) , (2) and (3) can be synthesized according to or in analogy to the methods described in DE 195 04 224. UVI 6974 is a cationic photoinitiator commercially available from Union Carbide.

The mixture exhibits the phase behaviour Ch 68.7 I.

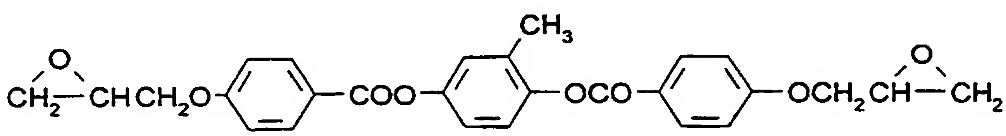
The mixture was coated onto a glass or plastic substrate and cured by irradiation with UV light to give a green cholesteric polymer film with a maximum reflection wavelength of 515 nm.

When the mixture was coated and polymerized on a polypropylene film substrate (50 µm thick), the resulting cholesteric polymer film showed such a strong adhesion that, when trying to release it from the substrate, the substrate tore before the cholesteric polymer film could be released.

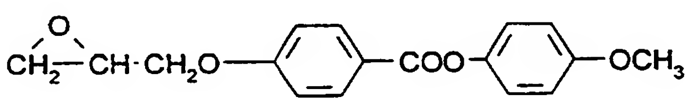
<u>Example 2</u>

The following mixture was formulated:

compound (1)	50.1 %
compound (4)	19.9 %
compound (5)	28.0 %
UVI-6974	2.0 %



(4)



(5)

Compounds (4) and (5) can be prepared as described in DE 195 04 224.

The mixture is green and shows the phase behaviour Ch 65.7 I.

The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants and/or operating conditions of this invention for those used in the preceding examples.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications of the invention to adapt it to various usages and conditions.

Patent Claims

1. A polymerizable composition comprising epoxy compounds, characterized in that it comprises the following components:

   a) component A comprising at least one chiral polymerizable mesogenic compound having a terminal polymerizable epoxy group,

   b) component B comprising at least one achiral polymerizable mesogenic compound having a terminal polymerizable epoxy group,

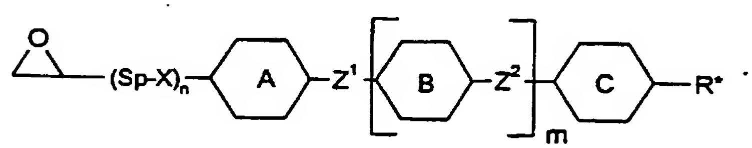
   c) optionally component C comprising at least one polymerizable mesogenic compound having two or more terminal polymerizable epoxy groups,

   d) optionally component D comprising one or more polymerizable non-mesogenic compounds having two or more terminal polymerizable epoxy groups,

   e) optionally component E comprising one or more chiral dopants, and

   f) an initiator component F comprising at least one polymerization initiator.

2. A composition according to claim 1, characterized in that component A comprises at least one compound of formula I:



in which

the rings A, B and C denote each independently 1,4-cyclohexylene, 1,4-cyclohexenylene or 1,4-phenylene being optionally substituted by one or two halogen atoms, cyano groups or alkyl, alkoxy or alkanoyl groups with 1 to 4 C-atoms that may be unsubstituted, mono- or polysubstituted by F or Cl,

Z^1 and Z^2 are each independently $-CH_2CH_2-$, -COO-, -OCO-, -CH=CH-COO-, -OCO-CH=CH-, -CH=CH-, $-OCH_2-$, $-CH_2O-$, -C≡C- or a single bond,

L^1 and L^2 are each independently H or F,

m is 0 or 1,

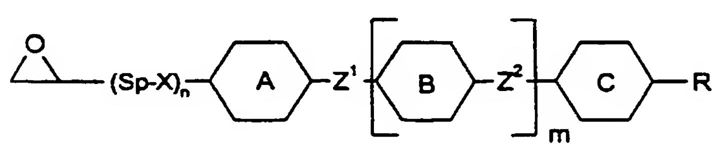
n is 0, 1 or 2,

Sp is a spacer group having 1 to 18 C atoms,

X is -O-, -S-, -CO-, -COO-, -OCO-, -O-COO-, -CO-S-, -S-CO- or a single bond,

R* is a chiral group having at least one chiral C atom.

3. A composition according to claim 1 or 2, characterized in that component B comprises at least one compound of formula II:

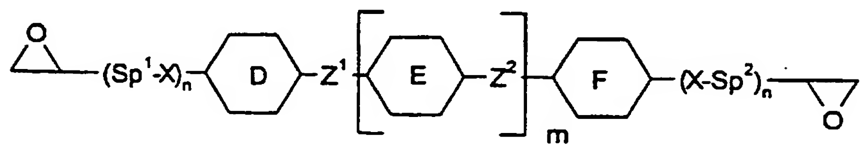


II

in which

A, B, C, Sp, X, Y, Z^1, Z^2, m and n have the meaning of formula I, and R is an achiral group having up to 16 C atoms.

4. A composition according to any of the claims 1 to 3, characterized in that component C comprises at least one compound of formula III:



III

in which

the rings D, E and F have one of the meanings given for the rings A, B and C in formula I, Sp^1 and Sp^2 each independently have one of the meanings given for Sp in formula I, and X, Y, Z^1, Z^2, m and n have the meaning given for formula I.

5. A composition according to claim 4 characterized in that Sp^1 and Sp^2 are different.

6. A composition according to any of the claims 1 to 5 characterized in that m is 1.

7. A composition according to any of the claims 1 to 6, characterized in that component F comprises at least one cationic photoinitiator.

8. A composition according to any of the claims 1 to 5, characterized in that it comprises

a) 2 to 75 % by weight of chiral component A,

b) 10 to 90 % by weight of achiral component B,

c) 0 to 60 % by weight of component C,

d) 0 to 20 % by weight of component D,

e) 0 to 15 % by weight of chiral component E, and

f) 0.01 to 10% by weight of component F.

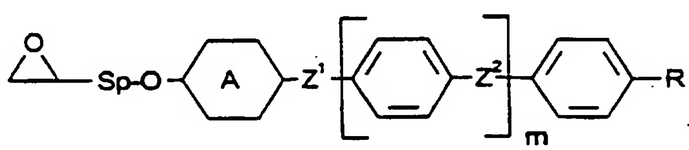
9. A polymerizable composition substantially as described in Example 1 or 2.

10. A crosslinked polymer obtained or obtainable by in-situ polymerisation of a composition according to any of claims 1 to 9.

11. Use of a composition as described in any of claims 1 to 9 for the preparation of a polymer or polymer film for use as a decorative pigment, electrooptical device, colour filter or adhesive, or in a security application.

12. A polymer or polymer film for use as a decorative pigment, electrooptical device, colour filter or adhesive, or in a security application,comprising a composition as described in any of claims 1 to 9.

13. An epoxy compound of formula IIa



IIa

wherein A, Z^1, R, n, m and Sp have the meaning of formula II and Z^2 is –COO- or a single bond, which can be used for a composition according to any of claims 1 to 9.

Application No: GB 9912054.5
Claims searched: 1-12

Examiner: Martin Price
Date of search: 11 October 1999

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.Q): C3P - PDA, PDY, PDZ; C3R - RSM, RPX

Int Cl (Ed.6): C08G 65/22; C09K 19/38

Other: Online - WPI, EPODOC, PAJ

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X,P	GB 2330360 A	(Merck) - see eg page 17 lines 10-16	1-12
X,P	GB 2329900 A	(Merck) - see eg page 27 lines 14-21	1-12
X,P	GB 2329899 A	(Merck) - see eg page 32 lines 15-20	1-12
X	GB 2315760 A	(Merck) - see eg page 9 lines 12-20	1-12
X	WO 97/35219 A1	(Merck) - see eg page 27 lines 24-30	1-12
X	WO 96/25470 A1	(Merck) - see eg claim 1	1-12
X	US 5560864	(Merck) - see eg claim 1 and examples 11-15	1-12

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.